

## PATENT ABSTRACTS OF JAPAN

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**(54) RECORDING SHEET AND RECORDED MATTER**

(57) Abstract:

**PROBLEM TO BE SOLVED:** To prevent fading when preserved after printing by incorporating a compound having 2,2,6,6-tetramethylpiperidine ring and a molecular weight of specific numeric value or below and a thiocyanate in a porous ink receiving layer.

**SOLUTION:** As a method for containing a hindered amine of a compound having 2,2,6,6-tetramethylpiperidine ring and a molecular weight of 1,000 or below, and a thiocyanate in a porous ink receiving layer, a method for giving by a method for dipping in a hindered amine and thiocyanate solution, a spraying method or the like or previously mixing the both is used. As contents of the amine and the thiocyanate, with a weight of the porous ink receiving layer as a reference, about 0.1 to 5 wt.% is best. As a total content of the amine and the thiocyanate, with a weight of the porous ink receiving layer as a reference, about 0.1 to 1 wt.% is best.

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**Notes:**

1. Untranslatable words are replaced with asterisks (\*\*\*\*).
2. Texts in the figures are not translated and shown as it is.

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Dictionary: Last updated 12/22/2006 / Priority: 1. Chemistry / 2. JIS (Japan Industrial Standards) term / 3. Mathematics/Physics

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## CLAIMS

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**[Claim(s)]**

**[Claim 1]** The sheet for record which has the porosity ink absorbing layer which has 2, 2, 6, and 6-tetramethylpiperidine ring, and contains a with a molecular weight of 1000 or less compound and thiocyanate on a base material.

**[Claim 2]** The sheet for record according to claim 1 which is the porous layer where a porosity ink absorbing layer contains hydrated alumina.

**[Claim 3]** The record thing with which it has the porosity ink absorbing layer which has 2, 2, 6, and 6-tetramethylpiperidine ring, and contains a with a molecular weight of 1000 or less compound and thiocyanate on a base material, and the pigment was supported by this porosity ink absorbing layer.

**[Claim 4]** The record thing according to claim 3 which is the porous layer where a porosity ink absorbing layer contains hydrated alumina.

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## DETAILED DESCRIPTION

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention relates to the sheet for record, and a record thing.

**[0002]**

**[Description of the Prior Art]** The picture is formed more often using various printers, such as an ink-jet method, an electrostatic image transfer method, and a sublimated type hot printing method. In this case, since absorptivity or resolution sufficient in ordinary paper are not obtained and a transparent thing is not obtained, either, the sheet for record in which the inorganic porous layer was formed on the base material is proposed, for example like JP,H2-276670,A.

[0003] The sheet for record which has the above inorganic porous layers has the good absorptivity of ink, and its fixability of a pigment is also good. However, if it was in the sheet for record which has this inorganic porous layer, there was a case where it faded after printing and during preservation.

[0004] In order to solve this problem, making the substance which has a fading prevention function contain in porosity is known. For example, to JP,H7-314882,A, giving fading tightness by making dithiocarbamate, a thiuram salt, thiocyanate, thiocyanate, hindered amine, etc. contain all over a porosity ink absorbing layer is indicated.

[0005]

[Problem(s) to be Solved by the Invention] The always more advanced thing is called for about the endurance of the record thing. This invention aims to let the absorptivity of ink obtain the sheet for record which the fixability of a pigment is a good sheet for record, and does not have fading even if saved after printing for a long period of time good.

[0006]

[Means for Solving the Problem] This invention offers the sheet for record which has the porosity ink absorbing layer which has 2, 2, 6, and 6-tetramethylpiperidine ring, and contains a with a molecular weight of 1000 or less compound and thiocyanate on a base material.

[0007] Moreover, this invention has the porosity ink absorbing layer which has 2, 2, 6, and 6-tetramethylpiperidine ring, and contains a with a molecular weight of 1000 or less compound and thiocyanate on a base material, and offers the record thing with which the pigment was supported by this porosity ink absorbing layer.

[0008] In this invention, it has 2, 2, 6, and 6-tetramethylpiperidine ring, and a with a molecular weight of 1000 or less compound is one sort of the compound called what is called hindered amine. On these Descriptions, this compound is called this hindered amine below. This compound functions as a fading inhibitor and fading of the ink under preservation after printing is prevented. Even if it is the compound which has 2, 2, 6, and 6-tetramethylpiperidine ring, when molecular weight exceeds 1000, it is difficult for a porous layer to make it support uniformly, and since a fading prevention function is not discovered enough, it is unsuitable.

[0009] Moreover, thiocyanate functions as a fading inhibitor similarly and fading of the ink under preservation after printing is prevented. As thiocyanate, sodium thiocyanate or potassium thiocyanate is desirable.

[0010] This invention discovers a high fading prevention function especially by using together this hindered amine and thiocyanate. Although the function of this fading inhibitor still is not clear, it is thought that other additives are stabilized or fading by the minute amount gas in the air is prevented.

[0011] The sheet for record of this invention is especially used preferably as a recording medium for ink-jet printers. It is because the absorptivity of ink and fixability are excellent, so

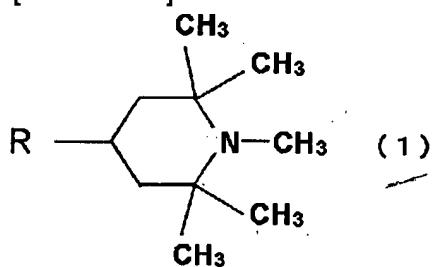
especially the sheet for record of this invention can express a clear color and the high depth of shade and can form a sharp dot.

[0012]

[Embodiment of the Invention] Since a little compounds which have an organic substituent appear in the 4th place of 1, 2, 2 and 6 which are expressed with a formula (1), and 6-pentamethylpiperidine ring as this hindered amine and a high effect is acquired, it is desirable. In a formula (1), R expresses an organic substituent.

[0013]

[Formula 1]



[0014] As a method of making a porosity ink absorbing layer containing this hindered amine and thiocyanate The method of giving the solution which dissolved this hindered amine and thiocyanate in the suitable solvent to the porosity ink absorbing layer formed beforehand with dip coating or a spray method is adopted preferably. The method of mixing this hindered amine and thiocyanate beforehand etc. is employable as the raw material which forms a porosity ink absorbing layer.

[0015] As content of this hindered amine, it is desirable that it is 0.01 to 10 weight % on the basis of the weight of a porosity ink absorbing layer. When not filling the content of this hindered amine to 0.01weight %, since there is a possibility that the effect of this invention may not be discovered enough and fading of ink may take place, it is not desirable. When the content of this hindered amine exceeds 10 weight %, since there is a possibility of checking the absorptivity of a porous layer, it is not desirable. The content of this more desirable hindered amine is 0.1 to 5 weight %.

[0016] As content of thiocyanate, it is desirable that it is 0.01 to 10 weight % on the basis of the weight of a porosity ink absorbing layer. When not filling the content of thiocyanate to 0.01weight %, since there is a possibility that the effect of this invention may not be discovered enough and fading of ink may take place, it is not desirable. When the content of thiocyanate exceeds 10 weight %, since there is a possibility of checking the absorptivity of a porous layer, it is not desirable. The content of more desirable thiocyanate is 0.1 to 5 weight %.

[0017] As content of the sum total of this hindered amine and thiocyanate, it is desirable that it is 0.01 to 10 weight % on the basis of the weight of a porosity ink absorbing layer. When not filling total content to 0.01weight %, since there is a possibility that the effect of this invention

may not be discovered enough and fading of ink may take place, it is not desirable. When total content exceeds 10 weight %, since there is a possibility of checking the absorptivity of a porous layer, it is not desirable. The content of the sum total of this more desirable hindered amine and thiocyanate is 0.1 to 1 weight %.

[0018] In this invention, a porosity ink absorbing layer is an inorganic porous layer which absorbs ink and can be established in the case of record. Since the thickness of a porosity ink absorbing layer has a possibility that a pigment cannot be supported enough but only printed matter with the low depth of shade may be obtained when it is too thin, it is not desirable. Conversely, since there is a possibility that the hardness of a porosity ink absorbing layer falls, or transparency may decrease and the transparency or textures of printed matter may be spoiled when too thick, it is not desirable. The thickness with a desirable porosity ink absorbing layer is 1-50 micrometers.

[0019] As for a porosity ink absorbing layer, it is desirable that it is the composition which combined the inorganic particle with the binder preferably. As the quality of the material of an inorganic particle, silica, alumina, or these hydrates are desirable. Also in these quality of the materials, boehmite is desirable especially. It is because a record thing with it is obtained using various kinds of recording methods in order to often adsorb a pigment alternatively, while the porous layer which consists of boehmite has good absorptivity. [ the high depth of shade and ] [ clear ] Here, boehmite is hydrated alumina expressed with the empirical formula of  $\text{Al}_2\text{O}_3$  and  $n\text{H}_2\text{O}$  ( $n=1-1.5$ ).

[0020] When a porosity ink absorbing layer contains boehmite, as for the content of the sum total of this hindered amine and thiocyanate, it is desirable that it is 0.05-50mg per \*\* boehmite 1g. The more desirable range is 0.1-20mg.

[0021] Since it has sufficient absorptivity that the pore structure is 3-20nm as an average pore radius, and a pore volume is 0.3 - 2.0 cc/g as a porosity ink absorbing layer containing boehmite and it is transparent, it is desirable. If the porosity ink absorbing layer which has the pore structure of this range is used, when a base material is transparent, what also has a transparent sheet for record will be obtained. When a base material is opaque, physical properties needed, such as the absorptivity of ink, can be given to the sheet for record, without spoiling the textures of a base material. In addition, measurement of pore volume distribution is based on a nitrogen adsorption-and-desorption method.

[0022] for manufacturing the boehmite porosity ink absorbing layer which has the above pore structures -- boehmite -- the method of applying the coating slip obtained by adding a binder to sol on a base material, and drying is desirable. As a means to apply, DAIKOTA, a roll coater, air knife coater, blade coater, rod coater, bar coater, etc. are preferably employable.

[0023] As a binder used for a porosity ink absorbing layer Organic substances, such as starch, its denaturation thing, polyvinyl alcohol and its denaturation thing, SBR (styrene-butadiene

rubber) latex, NBR (acrylonitrile-butadiene rubber) latex, hydroxy cellulose, and polyvinyl pyrrolidone, can be used. Since it has a possibility that the hardness of a porosity ink absorbing layer may become inadequate when there is little amount of the binder used, and it has a possibility that the amount of absorption of ink and the holding amount of a pigment may become low when there is conversely, about 5 to 50 weight % of its inorganic particle is desirable. [ too much ]

[0024] In this invention, various things can be used as a base material. For example, plastics, such as fluororesin, such as polyester, such as polyethylene terephthalate, polycarbonate, and ETFE, or paper can be used conveniently. Corona discharge treatment, an under coat, etc. can also be performed in these base materials in order to raise the bond strength of a porosity ink absorbing layer.

[0025]

[Example] 540g of water and isopropyl alcohol 676g were taught to glass reactors with a capacity of 2l., and solution temperature was heated at 75 degrees C with the mantle heater. Aluminum isopropoxide 306g was added agitating, and the hydrolysis was performed for 5 hours, holding solution temperature at 75-78 degrees C. Temperature up was carried out to 95 degrees C after that, 9g of acetic acid was added, and amalgam decomposition was held and carried out to 75-78 degrees C for 48 hours. Furthermore, this liquid was condensed until it was set to 900g, and white sol was obtained. The dry matter of this sol was boehmite.

[0026] The polyvinyl alcohol 1 weight part was added to this alumina sol 5 weight part, water was added further, and slurry of about 10% of solid content was prepared. On the base material which consists this slurry of polyethylene terephthalate (100 micrometers in thickness) which performed corona discharge treatment, it applied and dried and the porosity ink absorbing layer of the quality of boehmite was formed so that bar coater might be used and the layer thickness at the time of desiccation might be set to 30 micrometers.

[0027] About the coating side of the sheet for record obtained as mentioned above, impregnation treatment of the treatment drugs shown in Table 1 was performed. First, it sank into the 5-weight % toluene solution of this hindered amine shown in Table 1. However, only LX-332 of Table 1 applied this hindered amine by the aqueous emulsion contained 5weight %. Then, this was hung perpendicularly, it was air-dry, and stoving of the 140 degrees C was carried out for 4 minutes with the drum dryer. further -- next, it was immersed in the 3-weight % aqueous solution of sodium thiocyanate, after applying a solution uniformly, this was hung perpendicularly and it was air-dry, and stoving of the 140 degrees C was further carried out for 4 minutes with the drum dryer.

[0028] In Table 1, Examples 1-4 are comparative examples. Example 1 is an example which does not perform impregnation treatment by sodium thiocyanate and this hindered amine. Example 2 is an example which does not perform impregnation treatment by this hindered

amine. Examples 3 and 4 are examples which do not perform impregnation treatment by sodium thiocyanate.

[0029] In Table 1, in tinuvin 123, tinuvin 770, and tinuvin 144, it is this hindered amine and is the trade name of Tiba Speciality Chemicals, respectively.

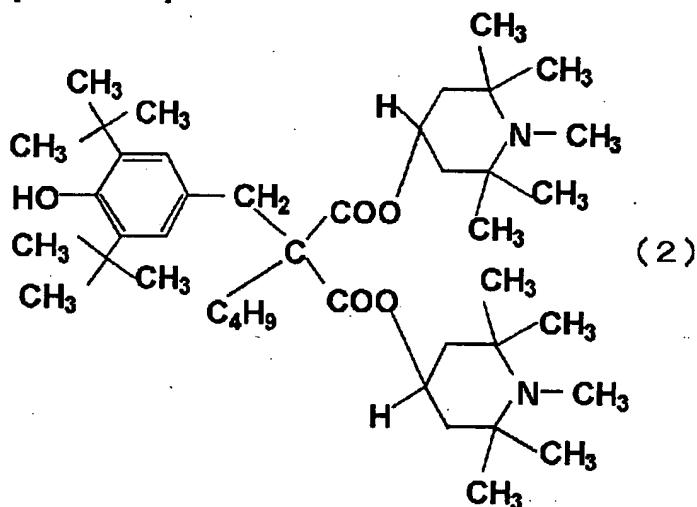
[0030] Specifically, tinuvin 123 is a sebacic acid screw (1-octyloxy 2, 2, and 6, 6-tetramethyl 4-piperidyl) (molecular weight 480).

[0031] Tinuvin 770 is a sebacic acid screw (2, 2, 6, and 6-tetramethyl 4-piperidyl).

[0032] Tinuvin 144 is a 2-[(3, 5-\*\*\*\*- 1, 1-dimethyl ethyl) -4-hydroxy phenylmethyl]-2-butyl malonic acid screw (1, 2, 2, 6, and 6-pentamethyl 4-piperidyl) (molecular weight 685). The constitutional formula of tinuvin 144 is shown in a formula (2).

[0033]

[Formula 2]



[0034] In Table 1, LA-52, LA-57, LA-62, LA-82, and LX-332 are this hindered amine, and are the part number of the hindered amine currently sold by Asahi Denka Kogyo K.K. by the trade name of the ADEKA stub, respectively.

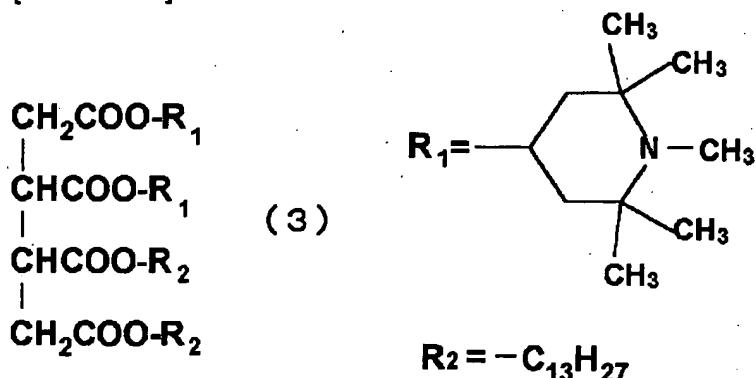
[0035] LA-52 are tetrakis (1, 2, 2, 6, and 6-pentamethyl 4-piperidyl)-1, 2 and 3, and 4-butane tetracarboxylate (molecular weight 847), and, specifically, are a compound shown by existing-chemical-substances number (5)-6116.

[0036] LA-57 are tetrakis (2, 2, 6, and 6-tetramethyl 4-piperidyl)-1, 2 and 3, and 4-butane tetracarboxylate (molecular weight 791), and are a compound shown by existing-chemical-substances number (5)-5555.

[0037] LA-62 are ester (average molecular weight 900) of 1, 2, 2, 6, and 6-pentamethyl 4-PIPERIJINORU and tridecyl alcohol, and 1, 2, 3, and 4-butane tetracarboxylic acid, and are a compound shown by existing-chemical-substances number (5)-5711. One sort of constitutional formulas of the compound contained in ADEKA stub LA-62 are shown in a formula (3).

[0038]

[Formula 3]



[0039] LA-67 are ester (average molecular weight 900) of 2, 2, 6, and 6-tetramethyl 4-PIPERIJINORU and tridecyl alcohol, and 1, 2, 3, and 4-butane tetracarboxylic acid, and are a compound shown by existing-chemical-substances number (5)-5755.

[0040] LA-82 are 2, 2, 6, and 6-tetramethyl 4-piperidyl methacrylate (molecular weight 239), and are a compound shown by existing-chemical-substances number (5)-6023.

[0041] LX-332 are the emulsification emulsion of hindered amine (average molecular weight 900) of LA-62, and are a substance shown by existing-chemical-substances number (5)-6116.

[0042] The processed sheet for record starts a part, and \*\*\*\* it in a hydrochloric acid aqueous solution or toluene for 12 hours, and quantitative analysis is carried out about an eluate with the absorption spectrometry method or ion chromatography by ultraviolet and a visible spectrum, The holding amount of thiocyanate in the sheet for record and this hindered amine was measured. A holding amount shows the holding amount per boehmite 100g by g.

[0043] "NaSCN / tinuvin 123" of the column of the treatment agent of Example 5 of Table 1 show that sodium thiocyanate and tinuvin 123 were used together. The holding amount of Table 1 expresses the holding amount per 100g of ink absorbing layers per g, for example, "2.2/4.1" in the column of the holding amount of Example 5 shows that the holding amount of sodium thiocyanate is [ the holding amount of tinuvin 123 ] 4.1g/100g in 2.2g/100g.

[0044] when it records on these sheets for record by using an ink-jet printer, the absorptivity of ink and the fixability of a pigment are -- also rubbing -- it excelled like the unsettled thing. Moreover, as for neither of the sheets for record, visually, coloring was accepted. After applying the black ink which contains the hood black 2 in these sheets for record, it was indoors exposed for 30 days and the grade of fading was investigated. The result is shown in Table 1 as fading nature. As for x, what the grade of fading is not accepted as for what has the large grade of fading, and \*\*, and the grade of fading is hardly accepted in as for an inner thing and O is shown.

[0045]

[Table 1]

例	処理剤	担持量	退色性
1	処理なし	0. 0	×
2	Na SCN	2. 4	△
3	チヌビン123	4. 0	△
4	LX-332	4. 3	△
5	Na SCN/チヌビン123	2. 2/4. 1	○
6	Na SCN/チヌビン770	2. 5/4. 1	○
7	Na SCN/チヌビン144	2. 4/3. 9	○
8	Na SCN/LA-52	2. 1/4. 0	○
9	Na SCN/LA-57	2. 4/4. 2	○
10	Na SCN/LA-62	2. 2/4. 1	○
11	Na SCN/LA-67	2. 3/3. 7	○
12	Na SCN/LA-82	2. 3/3. 7	○
13	Na SCN/LX-332	2. 4/4. 4	○

[0046]

[Effect of the Invention] The sheet for record of this invention has the good absorptivity of ink, and its fixability of a pigment is good. And fading does not produce long-term preservation, either. Although the sheet for record of this invention is effective in various recording methods, it fits the recording medium for ink-jet printers especially.

[Translation done.]